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(54) METHOD FOR MANUFACTURING TUBES BY CENTRIFUGAL CASTING

(71) We, CESKOSLOVENSKA AKADEMIE VED, a Czechoslovak Corporation, of No. 3 Národni, Praha 1, Czechoslovakia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of manufacturing tubes by centrifugal casting.

Centrifugal casting of tubes from molten metals, molten glass, concrete or plastics in solid rotating molds is known. This method requires accurate fixing of the tubular mold about the rotation axis thereof in order to obtain exactly centric tubes with uniform wall thickness. That can be accomplished by an exact mounting of the mold in bearings of the device for centrifugal casting. The mold must be newly adjusted with respect to the rotation axis for any newly chosen tube diameter.

According to the present invention there is provided a method of manufacturing tubes by centrifugal casting including placing casting liquid in a closed solid hollow mold, placing the mold and casting liquid into a larger rotatable container, the remaining space in the container being completely filled with a bearing liquid having a higher specific weight than the mean specific weight of the mold and of the casting liquid without regard to gas enclosed within the mold, and rotating the container, the casting liquid due to cooling down or due to some chemical reaction solidifying in the course of rotation of the container to form a tube. It is obvious that by the provision of different specific weights of the bearing liquid with respect to the mean specific weight of the mold and of the casting liquid an automatic centering of the mold with the casting liquid and an exactly tubular shape of the cast tube can be obtained, if a sufficient centrifugal acceleration is provided. The centrifugal acceleration should be higher than 10 g in order to produce uniform wall thickness of a cast tube, otherwise no exactly centric tubes are formed, as particularly dynamic influences on the mold and on the cast liquid in the mold prevent its exact centering. "g" is the gravity acceleration on the Earth surface, having the value of 981.017 cm/s². A number of influences can be observed in the course of casting, a discussion of such influences is however not entered into here as they have been already frequently described in different patent specifications, dealing with processes of centrifugal casting of tubes.

A constructional embodiment of the invention will now be described by way of example with reference to the accompanying drawing, which is a longitudinal part sectional view of an apparatus for performing the method according to the present invention.

Referring now more particularly to the drawing there is shown a solid rotatable tubular container 1 mounted in bearings 5. In this container 1 a certain amount of bearing liquid 3 is placed. The rotational movement is transmitted to the container 1 by a drive motor 6, for instance an electric motor with a gear case. The tubular container 1 is sealed at one end while at the other end it is provided with a removable cover 4, for instance a screw cap with a deaeration valve 7. A mold 2 floats during rotation of the container 1 in the bearing liquid 3, a certain amount of casting liquid being enclosed in the mold 2. The bearing liquid 3 covers the entire space of the container 1 beyond the mold 2.

The position of the rotatable container used for the centrifugal casting of tubes

according to this invention can be chosen arbitrarily so far as the centrifugal acceleration surpasses gravitation. The horizontal position is however advantageous, as it enables manufacture of tubes of equal diameter of any required length. The new method of centrifugal casting of tubes according to this invention enables an automatic centering of molds of different sizes using a simple and universally applicable arrangement. The only limitations are the prior chosen dimensions of the rotatable container, that is, its internal diameter and length. It is obvious that the maximum external diameter of the centered mold must be at least a sufficient amount smaller than the internal diameter of the rotatable container to allow floating of the centered mold on a layer of bearing liquid. There is therefore always a larger or smaller amount of bearing liquid in the rotatable container, which always fills the space between its internal wall and the mold.

Any sufficiently rigid tube made of a material which remains stable when in contact with the bearing liquid at casting conditions can be used for the rotatable container. Tubes of steel, iron, metal alloys, can be used and if desired may be clad interiorly with heat resistant material such as concrete, fireclay or graphite. Another suitable material is inorganic glass of various types. It is equally possible to adapt for this purpose some known arrangements for the centrifugal casting of tubes, particularly arrangements for discontinuous casting.

Any kind of liquid or molten material can be used as a bearing liquid provided its specific weight is higher than that of the mold completely filled with the casting liquid and the solidifying temperature of which is lower than the temperature at which the casting liquid is solidified, or the temperature of polymerisation of the casting liquid. Molten metals or metal alloys, mercury or other molten material can be used as the bearing liquid. The selection depends on the kind of casting liquid and on the material of the mold. If the condition of a lower specific weight of the filled mold is not fulfilled, disregarding the gas bubble forming the hollow part of the tube, with respect to the bearing liquid, the system becomes unstable and the axis of the mold can easily be diverted from the axis of the rotatable container with the bearing liquid. In such a case the mold can take up an inclined position in the rotatable container and the casting liquid, concentrated at both ends of the mold does not form a tube.

Both bearing and casting liquids can be prepared directly in the container or mold by melting granulated or otherwise comminuted material.

The casting liquid can be for instance molten metal, molten glass, molten thermoplastic polymers, liquid monomers and mixtures of monomers, which can polymerize en bloc, furthermore concrete mixture, mixture of plaster and water and similar material, solidifying either by changes of temperature or by chemical reaction, as long as they meet the condition that the mean specific weight of the mold and casting liquid is lower than the specific weight of the bearing liquid. It is obvious that the enumeratiion of these examples is not complete and the examples are mentioned solely for illustration of the wide range of choice of material suitable for casting.

The proper mold for centrifugal casting with automatic centering can be represented by any stiff tube made of material which is attacked neither externally by the bearing liquid, nor internally by the casting liquid. The tubes may be made of glass or flexible material such as polyethylene. These tubes should have a uniform wall thickness, the internal surface should be smooth and they should be straight along the whole length. For softer materials, polyethylene and similar materials a limited deflection along the whole length of the tube is of no consequence, particularly if the bearing liquid with a much higher specific weight than that of the material of the mold is chosen, as in the course of rotation at high rotational speed the tube is automatically longitudinally straightened with respect to the rotational axis. It is obvious that for rigid material such as glass, metal and similar materials the high stiffness would prevent any straightening. Known separating layers may be used for smoothing the internal surface of the molds or to enable an easier removal of cast products.

A precalculated amount of casting liquid is fed into the molds and the mold is closed. For smaller arrangements for centrifugal casting of tubes the filled and closed mold can be simply dipped below the level of the bearing liquid when the arrangement is in a vertical position and subsequently the container with the mold and the bearing liquid can be closed by a well fitting closure. For larger molds for which the force necessary for immersing the mold in the bearing liquid is too high the following method can be applied.

The filled and closed mold is placed into a empty container and the container is closed. The bearing liquid is now slowly supplied into the container by way of a couple of valves which both are open in the course of filling and which are placed at the highest point of the container. The filling is continued until the whole internal space of the container is full and all air has escaped via the deaeration valve. Then both valves are closed and the arrangement for centrifugal casting brought to rotation. The whole tubu-

lar container must be either heated or cooled during casting. The heating or cooling may be carried out e.g. by immersing the rotating container in a thermostatically controlled bath. Cooling has to be secured if a lowering of the temperatures is required, for metals, metal alloys, glass, thermoplastic polymers and similar materials. In other cases the rotatable container can be heated for example by a gas burner, by radiation, by a stream of hot gas or induction heating or electrical resistance heating.

If electrically conductive bearing liquids are used, such as low melting metal alloys, mercury and similar materials, induction heating may be advantageously applied, whereby the primary coils may be located around the rotatable container and the conductive liquid in the container is made to act as part of the secondary winding of an induction heating coil in the course of rotation. Both methods of electric heating, that is electrical resistance and induction heating enable easy regulation of the temperatures in the course of the whole casting process.

Although it is easy to establish the conditions for having the mold exactly coaxial with the rotatable container 1 (using the above mentioned rule that the average density of the solid mold and the casting liquid should be lower than that of the bearing liquid), it is, of course, possible to compute said conditions exactly, even the density of the gas in the mold being taken in account. Then any possible case can be computed even when the casting liquid is denser than the bearing liquid, i.e. when a solid hollow mold is used which is so much less dense than the casting liquid so that the average density of the casting liquid and mold is lower than that of the bearing liquid.

The computation starts from the fact that the mold rotating in the bearing liquid can take three different bearings:

1) the axis of the mold is parallel to but not identical with the rotation axis of the container; this case occurs if the density of the casting liquid and mold is higher than that of the bearing liquid. The mold is thus driven to the wall of the container.
2) The axis of the mold and the rotation axis of the container are intersecting; when the length of the mold is less than the inside diameter of the container, the axes will intersect at right angles, when not, the ends of the inner mold touch the wall of the container.
3) The axis of the mold and the rotation axis are identical.

For making tubes by centrifugal casting, only the case 3) is desirable. For securing said coincidence of axes, following two conditions are simultaneously to be fulfilled:

$$1)\quad \frac{\rho_2}{\rho_1} > k+\beta^2(1+\alpha-k)$$

$$2)\quad \frac{\rho_2}{\rho_1} > k\left[\frac{1-\xi^2\beta^2-6\alpha^2}{\xi^2-6}\right]+\beta^2\left[\frac{\xi^2-6\beta^2}{\xi^2-6}-\frac{\alpha^2\xi^2\alpha-6\beta^2}{\xi^2-6}\right]$$

wherein

ρ_1=density of the casting liquid,
ρ_2=density of the bearing liquid,
k;α;β;ξ are dimensionless constants characterizing the system and defined as follows:

$$k=\frac{\text{density of the mold}}{\text{density of the casting liquid}}$$

α=characteristic of the material of the tube to be molded;

$$\alpha=\frac{V_1}{V_1+V_2},$$

wherein

V_1=the volume of the gas bubble and V_2 is the volume of the casting liquid;

β characterizes the wall-thickness of the mold;

$$\beta=\frac{d}{D},$$

where

D=outside diameter and
d=inside diameter of the mold.

$$\xi=\frac{L}{2D},$$

wherein

L is the length of the mold in the direction of its main axis.

Usually, the second condition is fulfilled simultaneously with the first one.

Example 1.

The rotatable container was made of a steel tube having a length of 500 mm, an internal diameter of 30 mm and a wall thickness of 2.5 mm. The container was closed at one end by a disk of the same material, which was welded to the tube and was provided on the other end with a thread and a tight fitting screw cap. A part of the space of the container was filled with mercury, serving as the bearing liquid, the remaining space being taken up by the mold. The mold consisted of a glass tube of an internal diameter of 26 mm, the wall thickness being 1.2 mm, the length 495 mm. The mold itself was sealed at one end and after cooling down filled up to about half its volume with a monomeric mixture of the following composition:

80 per cent by volume of ethylene glycol-monomethacrylate containing 0.25 per cent by volume of ethylene glycol - di - methacrylate, 19 per cent by volume of aqueous solution of ammonium per-sulphate, 2 per cent by weight concentration, and 1 per cent by volume of dimethylaminoethylacetate. The remaining space in the mould was filled with oxygen-free carbon dioxide and the second end sealed. The mold was thereafter inserted, using the screw cap of the container, below the mercury level and the screw cap screwed on to the rotatable container so as to be perfectly tight. The electric motor of the apparatus was by means of a regulating transformer continuously brought to about 6000 rpm. The rotation time at room temperature was 30 minutes. The rotating movement was thereafter stopped, the mold removed from the apparatus, the glass tube opened by cutting off both ends and then immersed in water. Although the tube increased its volume due to swelling in water, it could be easily removed from the mold.

Example 2.

The process according to example 1 was repeated with the difference that a wrapped hose from knit polyethyleneterephthalate fibres of an inside diameter of about 25 mm was used for reinforcing the hydrogel tube.

Example 3.

The process proceeded as in example 1; as the bearing liquid mercury preheated to about 70°C was used. The monomer mixture was of the following composition: 84.7 per-cent by volume of ethylene glycol - di - methacrylate volume of ethylene glycol mono-methacrylate containing 0.15 per cent by, 15 per cent by volume of methylmethacrylate and 0.35 per cent by volume of di-isopropyl percarbonate. The polymerization proceeded during rotation within 20 minutes. The pre-heating of the support tube with its charge was fully sufficient and no additional heating was required. The polymer tube was released from the mold after having been soaked in water over-night.

Example 4.

The container 1 was manufactured from a steel tube, inside diameter 30 mm, length, 500 mm, wall thickness 2.5 mm, fitted in ball bearings 5. The container was closed at one end by welding and at the other by a screw-cap 4. It was filled to about 2/3 of its volume with mercury, heated to about 90°C. A mixture of bee-wax and paraffin (2:1), heated to 95°C, was added to the mold 2 which was inserted into the container 1. The container 1 was closed and brought gradually to rotation at 6000 rpm. During the rotation, the container was cooled by a spray of cold water (7°C) for about 25 minutes. Then the rotation was stopped. The mold 2 was removed from the container 1 and the cast tube having outside diameter 17.5 mm and wall thickness 1.5 mm was removed from the mold. The tube was smooth and even. The mold was made from glass or polyethylene.

Example 5.

The process according to Example 4 was repeated except that mercury was heated to 85°C and the wax mixture was replaced by a prepolymer prepared from the monomeric mixture of the following composition: 89.9 parts (by weight) of methyl methacrylate, 10 parts of dibutyl phthalate and 0.1 part of dibenzoyl peroxide. The whole was rotated for 45 minutes at 80°C. Thereafter the container was left to cool down slowly while rotated steadily for about one hour. Then the rotation was stopped and a solid polymer tube from transparent, slightly plastified poly(methyl methacrylate) was removed from the mold.

Example 6.

The process according to Example 4 was repeated except that the casting liquid was 50 ml of the following monomer mixture:

99.8 parts of ethylene glycol monomethacrylate (containing 0.25 percent by weight of ethylene glycol dimethacrylate), 0.1 part of dibenzoyl peroxide and 0.1 part of N, N-dimethyl p-toluidine. The remaining space in the mold was blown out and filled with carbon dioxide, the container was closed and rotated at 6000 r.p.m. for 40 minutes. Then the rotation was stopped and a hard polymer tube removed from the mold. It was soaked in water overnight. The resulting elastic soft hydrogel tube was utilizable as prosthetic material in surgery.

Example 7.

The process according to the preceding Examples 4 to 6 was repeated with an epoxy

resin p, p' - dihydroxy - di - phenylpropane and epichlorhydrin mixed with 7 weight percent of hexamethylene diamine serving as a setting agent. The container was heated during the rotation to 120°C by means of an adjusted gas-flame burner. The reaction lasted one hour. After having been cooled down to room temperature the rotating container was stopped and a solid tough polymer tube suitable e.g. as a former for winding up electronic coils, obtained from the mold.

Example 8.

In the process according to preceding Examples 4—7 a silicone rubber mixture, Dentaflex (Registered Trade Mark) with vulcanizing agents and catalyst was cast into the form of an elastic hose. The polymerization lasted 15 minutes at the room temperature.

Example 9.

The process according to Example 5 was repeated with sodium chloride aqueous solution saturated at the polymerization temperature as a bearing liquid, with the same result.

Example 10.

The process according to Example 5 was repeated with melted Woods alloy instead of mercury, with similar result.

Example 11.

The process according to Example 6 was repeated except that a wrapped hose from knit poly(ethyleneterephthalate) filaments, outside diameter 17 mm, was inserted in the mold. The hose was automatically centered when rotated and formed an integral part of the polymer tube. It is possible to use any textile insert from filaments specifically lighter than the bearing liquid used, provided that the hose has outside diameter only slightly smaller than the calculated inside diameter of the mold, since otherwise the textile insert would not be placed coaxially in the interior of the polymer tube.

Example 12.

The process according to Example 4 was repeated at the room temperature, with a slurry of plaster of Paris as casting liquid. The hardening was finished in 40 minutes. The finished tube was then air-dried in a drying box at 60°C and could itself be employed as a mold.

Example 13.

In the apparatus described in Example 4. Woods alloy was melted and kept at about 80°C. 65 g of granulated polycapronamide (nylon 6) was then poured into a mold which was tightly closed and inserted in the molten metal, and the remaining space blown with pure nitrogen. The container was then rotated, while the temperature was gradually increased up to 240°C. At said temperature, the rotation at 600 r.p.m. was continued for 10 minutes and then the temperature was gradually decreased by a spray of water till to about 80°C (the time required was about one hour). The rotation was then stopped and the finished polyamide tube removed from the mold.

Example 14.

The device described in Example 1 was modified so that the bearings were placed beyond the hot zone and cooled by a stream of air. The container 1 was then filled to 2/3 of its volume with a melted alloy of lead and tin (ratio 1:1 by weight) at 250°C. A sealed ampoule from lead glass, density 2.8, containing 100 g of aluminium swarf, was then introduced and the container closed tightly. The volume of the ampoule was 1/3 of the container inside volume. The container was heated to 680°C by means of a gas flame burner while rotating at 6000 r.p.m. Then the container was slowly cooled down to 250°C and the rotation stopped. The aluminium tube wrapped in a glass layer was removed and quenched with water till the glass burst and fell off. The aluminium tube thus obtained had uniform wall thickness.

Example 15.

Polyamide tube was made by introducing into a mold a solution of 0.1 part of sodium salt of 6-caprolactam and 0.35 p of N-acetyl caprolactam in 100 p. of anhydrous pure 6-caprolactam. The temperature in the container was raised to 190°C and the container was spun at 5200 r.p.m. The container was then cooled and the polyamide tube removed from the mold.

Example 18

Polyethylene capillary tube 1 m long, inside diameter 1 mm, wall thickness 0.5 mm, was filled with a mixture of 69.7% (weight) of ethylene glycol monomethacrylate (containing 0.25% by weight of the respective diester), 30% of glycerol and 0.3% of di-isopropyl percarbonate, so that about one half of the inside volume of the mold was left empty. One end of the polyethylene tube was previously sealed, the other end was sealed only after the remaining space having been blown with pure nitrogen in order to remove molecular oxygen. The sealed mold thus obtained, about 950 mm long, was inserted into an iron container 1 m long, inside diameter 6 mm, wall thickness 1.5 m, welded at one end, the whole remaining space being filled up with mercury. The full container was closed by means of a screw-cap and rotated at 7000 r.p.m. in a thermostated water bath at 65°C for 20 minutes. The polyethylene

tube was then taken out, opened at both sides by cutting off the sealed ends. The inner hydrogel tube had inside diameter 0.7 mm. A conductive thin cable (0.5 mm) was inserted into it and stretched and fixed so that it was positioned in the axis of the hydrogel tube. Then a liquid polysiloxane/catalyst mixture was sucked in and the mixture was left to cure at the room temperature, yielding an elastic electroinsulating layer round the conductive cable. Then the polyethylene was dissolved in hot benzene and the remaining hydrogel capillary with inserted conductor was repeatedly purified by boiling for several hours in re-distilled water which was many times exchanged. The catheter so created could be used in experimental surgery for recording bio-currents.

The instant process being based on physical phenomena, the sort of the casting liquid is not essential. Therefore, only several typical casting liquids were exemplified. It is, however, to be understood that the process of the invention is suitable for any casting liquid, either melted or not, that solidifies either by physical solidification upon cooling or by a chemical process of any kind.

British Patent Application No. 29352/72 (Serial No. 1306543) describes and claims a tube for use as a prosthesis tube having more than one coaxial layer.

WHAT WE CLAIM IS:—

1. A method of manufacturing tubes by centrifugal casting including placing casting liquid in a closed solid hollow mold, placing the mold and casting liquid into a larger rotatable container, the remaining space in the container being completely filled with a bearing liquid having a higher specific weight than the mean specific weight of the mold and of the casting liquid without regard to gas enclosed within the mold, and rotating the container, the casting liquid due to cooling down or due to some chemical reaction solidfying in the course of rotation of the container to form a tube.

2. A method as claimed in claim 1, wherein the casting liquid completely fills the hollow mold, the inner diameter of the cast tube being formed by contraction of the casting liquid under a centrifugal forces of at least 10 g.

3. A method as claimed in claim 1 or 2, wherein the tube is cast stepwise to form more than one coaxial layer.

4. A method as claimed in any one of claims 1 to 3, wherein the mold is heated by induction heating whereby the bearing liquid is formed from an electrically conductive material and forms part of the secondary winding of an induction heating device.

5. A method as claimed in any one of the preceding claims, wherein the casting liquid is formed by melting a solid material in the mold.

6. A method of manufacturing tube by centrifugal casting substantially as hereinbefore described with reference to the accompanying drawing.

7. A tube when manufactured by the method claimed in any one of the preceding claims.

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1306541 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*